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TRANSPARENT FILM WITH EXCELLENT ANTI-DROP LET AND BLOCKING
PROPERTIES

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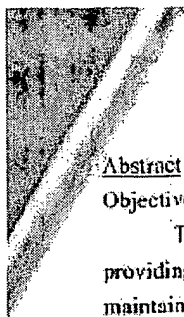
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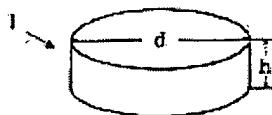
Abstract

Objective

To offer a film that maintains the excellent transparency of synthetic resin films while providing said film with high-level anti-droplet properties and good blocking properties, and maintaining these properties over a long period of time so that the film can be used in various fields, such as agriculture, book covers and commuter ticket covers.

Constitution

A layer of flat plate-form synthetic magnesium/sodium/lithium silicate particles (1) is laminated to at least one side of a synthetic resin film. The synthetic magnesium/sodium/lithium silicate particle layer endows the film of the present invention with hydrophilic properties (anti-droplet properties). Said particle layer is itself transparent, and thus does not block the transparency intrinsic to synthetic resin films. Consequently, the film of the present invention has excellent transparency. In addition, the synthetic magnesium/sodium/lithium silicate particles (1) are in contact with the synthetic resin film over the large surface areas of the plates, and said surfaces are active, so that the particles adhere firmly to said film and do not readily flow away.



Claim

A transparent film with excellent anti-droplet and blocking properties, comprising a synthetic magnesium/sodium/lithium silicate layer laminated onto at least one surface of a synthetic resin film.

Detailed description of the invention

[0001]

Industrial application field

The present invention relates to a transparent film with excellent anti-droplet and blocking properties, and specifically, relates to a film which is endowed with anti-droplet properties and blocking properties without compromising the transparency of a synthetic resin film that can be used in a wide variety of fields such as agriculture, book covers and commuter passes, and which also can maintain these desirable properties at a high level for a long period of time.



[0002]

Prior art

In the past, various types of synthetic resin films having excellent transparency and mechanical strength have been used in a wide variety of fields such as those described above. However, as is well known, synthetic resin films have hydrophobic surfaces and the films readily stick to each other, producing poor blocking properties. Consequently, when used as agricultural films, water vapor generated by the soil or produce condenses on the film surface due to its hydrophobic properties. This condensation decreases light transmissivity, having a detrimental influence on crop growth, or causing spoilage due to falling water droplets. Moreover, due to its poor blocking properties, problems occur with work operations around greenhouses and with opening and closing flaps for ventilation in greenhouses. In addition, when the materials are used as films for book covers, or as covers containing commuter passes, licenses or passports (referred to below as "general-purpose film"), problems with poor slip properties occur in addition to poor blocking properties, and smooth insertion and retraction of books, commuter passes, etc., is difficult.

[0003]

In order to endow synthetic resin films with good anti-droplet properties, resin containing a blended anti-droplet agent has been molded into film, or alternatively, technologies have been developed in which colloidal silica or alumina is adhered to the film surface (Japanese Kokai Patent Application Nos. Sho 55[1980]-56177, Sho 58[1983]-29831 and Hei 2[1990]-113939; referred to below as "anti-droplet technologies").

[0004]

On the other hand, in order to provide good blocking properties, technologies have been developed whereby silica, talc or other inorganic filler agents, or chemicals that bloom (indicating a phenomenon wherein the chemical gradually is drawn to the film surface as powder; for example, as with ethylene bis-stearamide) are kneaded into the synthetic resin film in the manner described above. Alternatively, technologies have been developed whereby an inorganic filling agent is adhered to the film surface by dusting or coating in order to provide irregularities on said film, thereby ensuring low blocking as a result of said irregularities (referred to below as "blocking improvement technologies").



[0005]

Problems to be solved by the invention

However, the following problems have occurred with the aforementioned anti-droplet technologies and blocking improvement technologies.

Anti-droplet technologies:

Anti-droplet agents are hydrophilic, and so an anti-droplet agent that is kneaded into a film will bleed to the film surface (phenomenon whereby material gradually exudes in liquid form at the surface). After blooming, the material can gradually flow away due to rain or condensed water from the aforementioned water vapor, and its effects will be prematurely lost. In addition, with technologies whereby colloidal silica or alumina is adhered to the film surface, the silica and alumina will readily wash away for the same reasons as above because they are hydrophilic, leading to the problem of being only temporarily effective. When these materials are used in conjunction with a binder, wash-away is prevented, but anti-droplet properties are hindered. Moreover, when colloidal silica is applied to a film surface and dried, the silica particles of the silica layer that is formed become microspheres. When pressure is applied as the film is wound into rolls at the time of molding, the microspheres are easily imbedded in the film, and the anti-blocking properties are thereby compromised. As a countermeasure, the combined use of the aforementioned blocking improvement technologies has been considered, but the following problems occur with the above blocking improvement technologies.

[0006]

Blocking improvement technologies

Inorganic fillers hinder film transparency because 1) they have different indices of refraction with respect to synthetic resin films, and 2) they have polygonal cross sections which cause scattering of light. Moreover, when inorganic fillers are applied to a film surface using a dusting powder, aventurine-like dust traces are formed at the film surface when the film is wound into rolls due to difficulties with uniform dusting, which causes a decrease in transparency and product value. In addition, the effects are not particularly good when inorganic filler is kneaded, and transparency is inhibited when large quantities are kneaded. Although inhibition of transparency is resolved when using a granular, spherical material of small grain diameter, blocking properties are not improved for the reasons described above. Conversely, if a material with a large grain diameter is used, blocking properties are improved, but transparency is hindered. Moreover, with technologies in which a resin containing blended inorganic filler is molded and drawn into film, the filler will separate from the film when the resin is formed into a thin film by drawing due to inferior adhesion between said filler and resin, resulting in fine gaps

at separation sites. Scattering of light occurs at these fine gap regions, and film transparency is greatly compromised by numerous gaps present over the entire film. This phenomenon similarly occurs during film drawing in technologies in which a paint containing blended inorganic filler is applied to a film surface.

[0007]

The present invention offers a technology that completely solves the above described problems with conventional technologies for endowing synthetic resin films with anti-droplet properties and improved blocking properties. With this technology, synthetic resin films can be endowed with effective anti-droplet properties and blocking properties while providing a film with superior transparency, and allowing long-term maintenance of the effectiveness of these properties.

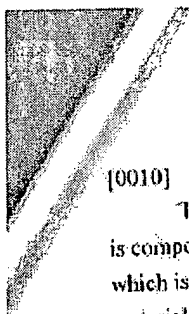
[0008]

Means to solve the problems

The inventors of the present invention, as a result of repeated investigations toward achieving the goals described above, found that when a special silicate compound that forms flat plates is used, superior anti-droplet properties and blocking properties can be obtained without compromising the transparency of a synthetic resin film, and in addition, that this material can be affixed with good adhesion to the surfaces of very smooth synthetic resin films, so that the material will not readily wash away due to water vapor condensation or droplets. The film of the present invention is based on this knowledge, and is characterized in that a layer of synthetic magnesium/sodium/lithium silicate as the aforementioned silicate compound is laminated to at least one side of a synthetic resin film.

[0009]

Examples of synthetic resins that constitute the base film for the film of the present invention include polyvinyl chloride, copolymers of vinyl chloride monomer and other monomers (for example, ethylene, propylene, vinyl acetate, vinylidene chloride, acrylic acid, acrylate ester methacrylic acid, methacrylate ester, maleic acid, fumaric acid and acrylonitrile), blends of these resins and other vinyl chloride resins, polyethylene, ethylene-vinyl acetate copolymer, polypropylene, polyester, polycarbonate, polymethyl methacrylate and various other synthetic resins that have been used in the past as agricultural films and general-purpose films.

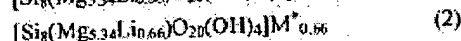
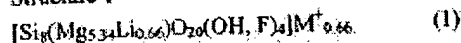


[0010]

The synthetic magnesium/sodium/lithium silicate that is laminated onto the base film that is composed of an aforementioned synthetic resin can have a structure that resembles hectorite, which is a natural mineral, and is represented by general formulas (1) and (2) below. This material consists of fine particles (1) having the form of flat plates as shown in Figure 1.

[0011]

Structure 1



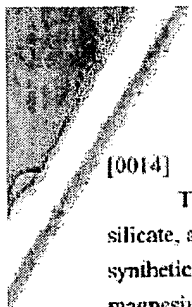
Where M denotes Na.

[0012]

This synthetic magnesium/sodium/lithium silicate preferably is a material wherein the primary particle plate diameter (represented by d in Figure 1) is about 20-500 nm, with about 20-100 nm being preferred, and the height (represented by h in Figure 1) is about 1 nm.

[0013]

The synthetic magnesium/sodium/lithium silicate aggregates into large secondary plate-form aggregates when in dry form, but when dispersed in water, the substitutable sodium ions are hydrated and diffuse into the water, so that the surfaces of the plates become negatively charged as shown in Figure 2. As a result, there is a repulsion between the grains (1), and the material is dispersed into primary grains, thus forming a transparent colloid. At this time, the edges of the plates, as shown in the figure, take on positive charge due to the cation (indicated by L in the figure) adsorption characteristics of said grains. When the concentration of the synthetic magnesium/sodium/lithium silicate is low, the negative charge at the plate surfaces is greater than the positive charge at the edges, so repulsion is strong, making it difficult for the grains to associate. In contrast, the grains are close to each other when the synthetic magnesium/sodium/lithium silicate concentration is high (or in other words, when the concentration of ions in the water is high), and the negative charges at the plate surfaces and positive charges at the edges attract each other, leading to binding. As a result, card structures of the type shown in Figure 3A and 3B are formed, leading to a gel condition. When the synthetic magnesium/sodium/lithium silicate concentration is additionally increased, the plate surface negative charge decreases, and plate surface-to-edge binding is also weakened, leading to aggregation of grains due to Van der Waals forces and loss of transparency.



[0014]

The present invention employs the properties of this synthetic magnesium/sodium/lithium silicate, and involves the lamination of this material to a synthetic resin film as a layer of synthetic magnesium/sodium/lithium silicate of low concentration. Specifically, synthetic magnesium/sodium/lithium silicate that has been uniformly dispersed in water; a mixture of alcohol and water, or an emulsion (all referred to below as "dispersion media"), at a concentration of 0.1-5 wt%, with 0.3-2.0 wt% being preferred, is applied and dried on the surface of a synthetic resin film by gravure coating, rod coating or other coating means at an application thickness of 0.03-3.0 g/m [sic] (dry thickness), with 0.15-1.5 g/m (dry thickness) being preferred.

300 mg/cm²
 wt. 1-5 g/m²

[0015]

With the synthetic magnesium/sodium/lithium silicate layer produced on the synthetic resin film in this manner, the particles do not assemble as shown in Figure 3, but rather, adhere to the film surface in primary particle form. Consequently, said particle layer itself has excellent transparency, and does not block the transparency of the synthetic resin film. If the concentration of the synthetic magnesium/sodium/lithium silicate in the dispersion medium is too low, numerous applications will be required in order to obtain the above application thickness, which is inefficient. On the other hand, if this concentration is too high, it will not be possible to obtain a transparent synthetic magnesium/sodium/lithium silicate layer. If the coating thickness is greater than indicated above, a non-transparent layer will be produced, whereas if the thickness is too small, the amount of adhered synthetic magnesium/sodium/lithium silicate will be insufficient, and the anti-droplet properties and blocking properties will be poor.

[0016]

In the dispersion media described above, methyl alcohol, ethyl alcohol, propyl alcohol and other alcohols can be used as the alcohol of the water-alcohol mixture. These alcohols have qualities whereby they improve coating properties. If the amount of alcohol is too small, there will be no effect, whereas if the amount is too great, gel formation will result. In the present invention, the alcohol is used at 1-50 parts by weight with respect to 100 parts by weight of water, with 2-10 parts by weight being preferred. Examples of emulsions include substances that are commonly used such as acrylic and urethane systems. Moreover, in order to improve wetting with respect to the base, surfactant can also be added. In this case, it is preferable to use a nonionic surfactant because the aforementioned particles are charged. The resin used in these emulsions has the effect of an adhesive at the time when the synthetic magnesium/sodium/lithium silicate particles are affixed to the surface of the synthetic resin film. If the resin content is too low, this effect will be lost, whereas if the content is too high, it will be

difficult to sufficiently manifest good blocking prevention properties. In the present invention, the substance is used at 1-15 NV% (normal volume %), with 3-10 NV% being preferred.

[0017]

Thus, the synthetic magnesium/sodium/lithium silicate particles are flat plates as shown in Figure 1, and the plate surfaces are charged negatively in the above dispersion media as shown in Figure 2. As a result, a strong coating film is formed on flat synthetic resin films due to the activity of the plate surfaces that presumably results from this charge, along with the large surface area of said plate surfaces. The synthetic magnesium/sodium/lithium silicate particles that are firmly adhered thus form uneven regions on the surface of the smooth synthetic resin film, and eliminate the tacky feeling from said film, thus endowing the film with good blocking properties.

[0018]

In the present invention, anti-droplet agents can be added beforehand to the aforementioned base film, examples of which include sorbitan monostearate, sorbitan monopalmitate, sorbitan monobehenate and other sorbitan-based surfactants, glycerin monolaurate, glycerin monostearate and other glycerin-based surfactants, polyethylene glycol monostearate, polyethylene glycol monopalmitate and other polyethylene glycol-based surfactants, and alkyl phenol alkylene oxide addition products. There will be no effect if the amount of anti-droplet agent used is too small, whereas costs will increase if the amount is too large. Consequently, in the present invention, it is appropriate to use an amount of about 0.5-5 PHR (abbreviation for "parts per resin"; for example, the blend ratio taking the amount of PVC as 100), with 1.5-2.5 PHR being preferred. Various types of chemicals can also be added to the base film in ranges in which transparency is not compromised (for example, ultraviolet absorbers, light stabilizers, anti-fog agents, antioxidants, colorants, anti-mold agents, flame retardants, stabilizers and lubricants).

[0019]

Operation of the invention

With the film of the present invention, the synthetic magnesium/sodium/lithium silicate that is laminated to at least one side is intrinsically hydrophilic, and thus provides hydrophilic properties (small water contact angle). Consequently, when water vapor generated by soil or produce condenses on the film of the present invention, water droplets are not formed, and moreover, the water droplets join together to form a film of water. Moreover, the aforementioned particles of synthetic magnesium/sodium/lithium silicate that are adhered to the surface of the

film of the present invention form uneven regions on said surface, and eliminate the tacky feel of the base film. By providing these uneven regions and eliminating the tacky feel, the film of the present invention is endowed with good blocking properties.

[0020]

In addition, the synthetic magnesium/sodium/lithium silicate particles do not aggregate together, but remain in the primary particle state. As a result, a good dispersed condition is maintained, and the material can be uniformly affixed to the synthetic resin film surface to form a particle layer. Consequently, the intrinsic transparency of the particles is not lost in the particle layer. Although the reason is unclear, in spite of the difference in the index of refraction between said particles and synthetic resin film, the film of the present invention maintains high transparency without loss of the superior transparency intrinsic to synthetic resin films.

[0021]

Thus, the synthetic magnesium/sodium/lithium silicate particles, as described above, ensure a large surface area of contact between the flat plate surfaces of said particles and the base film, and also provide a strong adhesive strength with the base film due to activity presumed to result from the negative charge at the surfaces of said plates. For this reason, with the film of the present invention, a synthetic magnesium/sodium/lithium silicate particle layer is formed that adhere with high strength to the smooth synthetic resin film surface. As a result, the layer has superior durability and does not readily flow away due to water vapor condensation or rain droplets.

[0022]

Application examples

Application Example 1

A coating having the composition shown in Table 2 was applied with a rod coater at a dry coating thickness of 0.3 g/m to both surfaces of a base film with a thickness of 0.1 mm composed of a resin blend having the composition shown in Table 1. After drying for 1 min at 100°C, a synthetic magnesium/sodium/lithium silicate particle layer has been laminated thereupon to obtain film (1) of the present invention appropriate for general-purpose use.

[0023]

Table 1

PVC (average degree of polymerization: 1300)	100 parts by weight
DOP (plasticizer)	45 parts by weight
TCP (plasticizer)	7 parts by weight
Epoxified soy oil (plasticizer)	2.0 parts by weight
Ca-Zn stabilizer	2 parts by weight
Methylene-bis-stearamide (lubricant)	0.02 part by weight

[0024]

Table 2

Water	100 parts by weight
Ethyl alcohol	10 parts by weight
Synthetic magnesium/sodium/lithium silicate (Nippon Silica Kogyo; product name Labonite RD; plate diameter (d in Figure 1): 20-30 nm, height (h in Figure 1): 1 nm)	1 part by weight
Nonionic surfactant (Polyoxyethylene nonylphenyl ether, manufactured by Nippon Yushi; product name Nonion NS-202)	0.1 part by weight

[0025]

Film (1) of the present invention obtained as described above was evaluated in terms of anti-droplet properties, blocking properties and transparency using the evaluation categories and criteria shown in Tables 3-5. The results are shown in Table 11.

[0026]

Table 3

Evaluation of anti-droplet properties

The film was suspended over a warm water bath at 35°C, and was transferred to a room at 15°C where it was left for 30 days. The water droplet adhesion condition of said film was then evaluated visually according to the following criteria.

○: Wetted with a film of water

□: Some droplets, but generally wetted in film form.

△: Fair number of adhered water droplets.

X: Water droplets adhered over entire surface

[0027]

Table 4

Evaluation of blocking prevention (slip properties)

Paper was layered to form an A4 size magazine, and after cutting film pieces, a welding process was carried out to produce a book cover. The ease of insertion and removal of the magazine was evaluated.

O: Smooth sliding was possible without any particular resistance.

□: Smooth sliding without any practical problems.

△: Not very smooth; sliding difficult from a practical standpoint.

X: Sliding difficult.

[0028]

Table 5

Evaluation of transparency

The boundary between the coating and uncoated surface was observed visually and evaluated according to the following criteria.

O: No boundary seen.

□: Boundary seen, but the same transparency was observed in the coating and uncoated surface.

△: Boundary clearly seen, and scattering seen with coating, leading to whitening.

[0029]

Comparative Example 1

2.0 PHR of talc (average particle diameter 5 μm) was added to the base film resin blend shown in Table 1 of Application Example 1, and the material was drawn 3x to produce a 0.1 mm comparative film (1). This comparative film (1) was evaluated in terms of anti-droplet properties, slip properties and transparency in the same manner as in Application Example 1, and the results are compiled in Table 11.

[0030]

Application Example 2

A coating having the composition shown in Table 7 was applied using a rod coater at a dry thickness of 0.7 g/m to both surfaces of a 0.1-mm base film composed of a resin blend having the composition shown in Table 6. After drying for 1 min at 120°C, a synthetic magnesium/sodium/lithium silicate particle layer was laminated thereupon to obtain film (2) of the present invention appropriate for agricultural use.

[0031]

Table 6

PVC (average degree of polymerization: 1300)	100 parts by weight
DOP (plasticizer)	46 parts by weight
TXP (plasticizer)	5 parts by weight
Epoxy resin (plasticizer)	2.0 parts by weight
Ba-Zn stabilizer	1.5 parts by weight
Methylene-bis-stearamide (lubricant)	0.2 part by weight
Sorbitan monopalmitate (anti-droplet agent)	2.0 parts by weight
Fluorine-system surfactant	0.2 part by weight
(Product name Sarflone S-393, manufactured by Asahi Glass)	

[0032]

Table 7

Acrylic emulsion (NV 5%)	100 parts by weight
Synthetic magnesium/sodium/lithium silicate (same as substance used in Application Example 1)	1.0 part by weight
Nonionic surfactant (same as substance used in Application Example 1)	0.1 part by weight

[0033]

Film (2) of the present invention obtained as described above was evaluated in terms of anti-droplet properties in the same manner as in Application Example 1. The blocking properties and transparency were evaluated by the evaluation criteria and methods described in Tables 8 and 9, and the results are compiled in Table 11.

[0034]

Table 8

Evaluation of Transparency

The various films were spread on a small tunnel-shaped greenhouse with a height of 1 m, and a plate with text written on it was placed in the tunnel (print size 3 cm square). Blurring was observed from outside the tunnel.

⊙: Text clearly visible.

○: Text was blurry, but easily read.

△: Text could not be read.

X: Presence of text unclear.

[0035]

Table 9

Evaluation of blocking properties

The film on the side wall of tunnel structure was opened in the morning, and the blocking properties were evaluated by the level of tackiness when closed in the evening. Evaluation was carried out according to the following criteria.

⊙: Slight tackiness, closed with minimal force.

O: Some tackiness; readily closed.

△: Tackiness, difficult to close.

X: Highly tacky, time required for closing.

[0036]

Comparative Example 2

A paint having the composition shown in Table 10 was applied to both sides of the base film used in Application Example 2 under the same conditions as in Application Example 2, and the paint was dried to obtain comparative film (2). The anti-droplet properties, blocking properties and transparency of comparative film (2) were evaluated in the same manner as in Application Example 2, and the results are shown in Table 11.

[0037]

Table 10

Acrylic emulsion (NV 5%)	100 parts by weight
Silica powder	1.5 parts by weight
(Product name Aerogel #300, manufactured by Nippon Aerogel)	
Nonionic surfactant	0.1 part by weight
(same as material used in Application Example 1)	

[0038]

Table 11

		②		
	①	防滴性	ブロッキング性	透明性③
④	本発明フィルム①	△	○	○
⑤	比較フィルム①	×	□	△
⑥	実施例①のベースフィルム	×	×	□
⑦	本発明フィルム②	◎	△	□
⑧	比較フィルム②	○	○	○
⑨	実施例②及び比較例②のベースフィルム	□	×	○

- Key: 1 Anti-droplet properties
 2 Blocking properties
 3 Transparency
 4 Film (1) of the present invention
 5 Comparative film (1)
 6 Base film of Application Example 1
 7 Film (2) of the present invention
 8 Comparative film (2)
 9 Base film for Application Example 2 and Comparative Example 2

[0039]

As is clear from Table 11, the films (1) and (2) of the present invention exhibited good anti-droplet properties, blocking properties and transparency. Comparative film (2) had good anti-droplet properties and transparency, but was found to have low blocking resistance.

[0040]

Effects of the invention

As described above, the present invention can endow synthetic resin films with good anti-droplet properties and blocking resistance without any loss in the transparency intrinsic to said films. Moreover, these described properties can be retained at a high level over long periods of time. As a result, the film of the present invention allows for smooth insertion and removal of a book or commuter pass when it is used as a general-purpose film for book covers or commuter pass covers. In addition, when used as an agricultural film, the film has the effect of facilitating greenhouse operations and the opening or closing of flaps for ventilation in greenhouses.

Brief description of the figures

Figure 1 is a diagram that elucidates the form of the synthetic magnesium/sodium/lithium silicate particles used in the film of the present invention.

Figure 2 is an explanatory diagram presenting the charged condition of the synthetic magnesium/sodium/lithium silicate particles of Figure 2 [sic; Figure 1] in water.

Figure 3, a diagram showing interactions between the synthetic magnesium/sodium/lithium silicate particles shown in Figure 1.

Explanation of symbols

- 1 Synthetic magnesium/sodium/lithium silicate particles



Figure 1

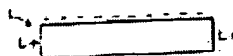


Figure 2

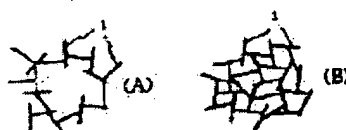


Figure 3